

Interaction between Cr(VI) and a Fe-rich soil in the presence of oxalic and tartaric acids

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Abstract This study examined the interaction between Cr(VI) and a Fe-rich soil in the presence of low-molecular-weight organic acids as a function of pH. Oxalic and tartaric acids were chosen since they existed in soils commonly. Batch experiments showed that adsorption of Cr(VI) by the soil within the pH range examined was inhibited in the presence of oxalic acid, which was more pronounced when the initial ratio of [oxalic acid]/[Cr(VI)] was raised from 1:1 to 2:1. With the addition of tartaric acid, concentration of Cr(VI) in equilibrium solutions was far less than that of single adsorbate system across the pH wide (2.5–5.5), which was noticeable especially at low pH. The results were attributed to Cr(VI) adsorption and, particularly, the soil surface catalyzed reduction of Cr(VI) to Cr(III) by tartaric acid. The data reported in this paper suggested that the mobility, the bioavailability, and the toxicity of Cr(VI) in soil environments might be greatly affected by pH, the presence and nature of low-weight-molecular organic acids (oxalic and tartaric acids).

Keywords Cr(VI) · Fe-rich soil · Adsorption · Reduction

Introduction

The contamination of soils and aquatic environments by Cr has attracted considerable attention over the last years due to high levels of Cr waste released from a large variety of

industrial processes. Cr(III) and Cr(VI) are two thermodynamically stable oxidation states of chromium present in natural soils, and their geochemical and biologic behaviors are drastically different (Kotaś and Stasicka 2000). Cr(III) is known to be relatively non-toxic and weakly mobile in soils, while Cr(VI) is highly toxic and commonly very mobile. Accordingly, reduction of Cr(VI) to Cr(III), and subsequent precipitation of Cr(III) is the most common method of minimizing Cr(VI) mobility.

Cr(VI) could be reduced by many reductants present in soils, such as organic C-based materials, Fe(II) and sulfide (Fendorf 1995), which could be potentially used in remediation of Cr(VI) contamination. The utilization of organic materials is more environmentally beneficial because they would not exhibit toxicity themselves and introduce additional environmental problems. However, reduction of Cr(VI) by organic compounds was very slow (Wittbrodt and Palmer 1996). The presence of clay minerals and hydrous oxides, such as TiO₂, γ -Al₂O₃, α -FeOOH, has been confirmed to be capable of catalyzing Cr(VI) reduction by organic compounds (Deng and Stone 1996a, 1996b; Deng et al. 2003; Tzou et al. 2003). These studies have also indicated that surface-catalyzed Cr(VI) reduction might occur in soils, while the mechanisms have not been carefully examined till date.

Oxalic and tartaric acids are organic acids existing ubiquitously in soil solutions (Jones 1998), which could affect geochemical behavior of Cr(VI) in soils through competitive adsorption for reactive surface sites or redox reactions involving soils. Therefore, the purposes of this research were to examine the influence of organic acids on Cr(VI) adsorption by a Fe-rich soil as a function of pH and to assess whether Cr(VI) reduction by organic acids could be catalyzed by the soil surfaces. The red soil was selected because it is widely spread in south China and it has high

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contents of Fe oxides. Results obtained from the whole soil would be more helpful when developing remedial techniques for chromium site remediation.

Materials and methods

The Fe-rich soil sample was collected from the 100- to 120-cm layer of red soil in Gaoan County (115°0′–115°34′E, 28°02′–28°38′N), Jiangxi Province, air-dried, and ground to pass 100-mesh sieve prior to being used in this study. The depth was pre-selected because the content of soil organic matters (SOM) was very low in this layer so that the interaction between Cr(VI) and soil organic matters could not be considered. Soil pH measurement was made in H₂O at 1:2.5 (w/v) soil solution ratio using a pH glass electrode. Organic carbon was determined according to the Walkley and Black wet oxidation procedure (Nelson and Sommers 1996). Organic matter concentration of the soil was taken to be organic carbon concentration multiplied by 1.724. The cation exchange capacity (CEC) was determined by 1.0 M NH₄OAC buffered at pH 7 (Chapman, 1965). Dithionate-citrate-bicarbonate extractable Fe was measured according to the method of Mehra and Jackson (1960). Amorphous or poorly Fe oxides were determined by extracting 1 g of soil in 30 mL of acidified ammonium oxalate buffer [0.175M (NH₄)₂C₂O₄ + 0.1M H₂C₂O₄, pH 3.0] for 2 h (Loepper and Inskeep 1996). To analyze the total dissolved iron in extracts, hydroxylamine hydrochloride was first added to reduce Fe³⁺ to Fe²⁺ in samples, and then concentration of Fe²⁺ was measured using 1,10-phenanthroline method. The selected properties of the soil are presented in Table 1. All solutions and suspensions were prepared using deionized water. All the glassware were soaked in 5% HNO₃ overnight and then thoroughly rinsed with deionized water prior to use. Analytical reagent grade chemicals were used for preparation of all solutions throughout the study. Stock solution containing 0.01 M Cr(VI) was prepared from K₂CrO₄, and organic acids stock solutions were prepared daily.

Batch experiments involved adding 1.000 g of the soil into a 50-mL plastic tube, followed by sequential addition of an organic acid and Cr(VI) to a total volume of 30 mL with 0.01 M NaNO₃ as background electrolyte. Initial suspensions contained 0.1 mM Cr(VI) with the organic

Table 1 Selected properties of the soil used in this study

pH	SOM (g kg ⁻¹)	Fe _d (g kg ⁻¹)	Fe _{ox} (g kg ⁻¹)	CEC (mmol kg ⁻¹)
4.5	3.76	14.95	1.51	26.3

Fe_d: Dithionate–citrate–bicarbonate extractable Fe

Fe_{ox}: Fe extracted by acidified ammonium oxalate buffer

acid concentration of 0, 0.1 or 0.2 mM, oxalic acid and 0 or 0.1 mM tartaric acid. Solution pH ranging from 3.00 to 6.00 was obtained by adding 0.1 or 0.01 M HNO₃ or NaOH. Each tube was then sealed and shaken at room temperature (25–30°C) for 24 h. After pH of the suspension was measured, the solution was separated from the solid phase by centrifugation at 4,000 rpm for 10 min. The concentration of Cr in solutions was measured with flame atomic absorption spectrophotometer for total Cr and the colorimetric analysis for Cr(VI) using 1,5-diphenylcarbazide indicator (James and Barlett 1983). Cr(III) was calculated as the difference between total Cr and Cr(VI). Adsorbed Cr(VI) was calculated from the difference between the Cr(VI) initially added to the system and that remaining in the solution after equilibration. All the experiments were triplicated, and the mean values were presented.

Results and discussion

Interaction between Cr(VI) and the soil in the presence of oxalic acid

As shown in Fig. 1, in the absence of oxalic acid, the decrease in adsorption of Cr(VI) by the soil with the increase in pH was observed. This is because the amphoteric Fe-rich soil surfaces typically would bear more negative charges with the increase in pH, then adsorption of oxyanions like CrO₄²⁻ onto the soil would be inhibited by electrostatic repulsion. Additionally, direct reduction of Cr(VI) by the soil components could be precluded because the soil used

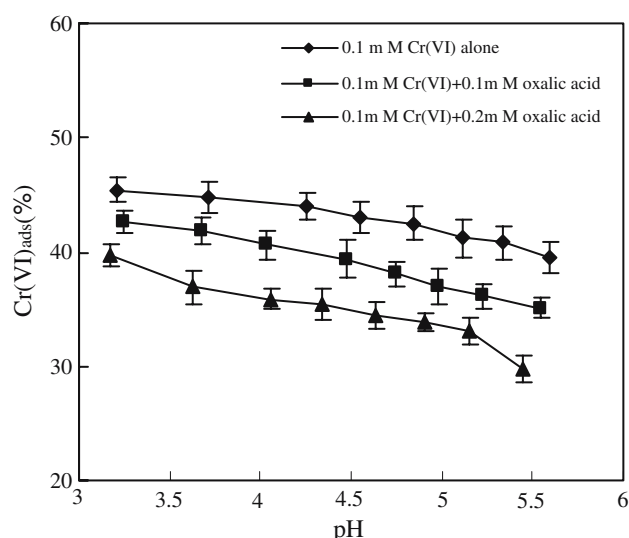


Fig. 1 Interaction between Cr(VI) and the soil in the presence of oxalic acid

in the study was highly weathered. So the observed decrease in $[Cr(VI)]_{aq}$ could only be attributed to its adsorption onto soil surfaces in the absence of organic acids, which was in agreement with previous study (Zhou et al. 2001).

As shown in Fig. 1, when coexisting with oxalic acid, Cr(VI) adsorption by the soils was decreased with more Cr(VI) existing in solutions, which was more pronounced as the initial concentration of this competitive anion was increased from 0.1 to 0.2 mM. Previous studies have also shown that the adsorption of chromate onto goethite was diminished in the presence of oxalate (Mesuers and Fish 1992). Oxalic acid may exert influence on Cr(VI) adsorption through competition for binding sites with Cr(VI) species or through the alteration of surface properties of the soil. Studies have confirmed that adsorption of oxalic acid onto Fe oxide surfaces through formation of inner-sphere complexes (Persson and Axe 2005), so oxalic acid might also associate with surface functional groups on surfaces of the soil minerals such as Fe oxides, forming strong inner-sphere surface complexes. However, adsorption of Cr(VI) by clay minerals was often regarded through electrostatic attraction with out-sphere complex formation (Zachara et al. 1988; Fritzen et al. 2006). Additionally, the presence of oxalate would result in more negative surface charge of the Fe-rich soils and a decrease in ζ potential (Xu et al. 2003, 2004), leading to the increase in electrostatic repulsion between Cr(VI) and the negatively charged surface sites. Therefore, the two mechanisms described above jointly resulted in the inhibition of Cr(VI) adsorption by the soil in the presence of oxalic acid.

Interaction between Cr(VI) and the soil in the presence of tartaric acid

In addition to two carboxylic acid groups, tartaric acid also possesses two α -hydroxyl function groups, thereby leading to reactions occurring in the soil–Cr(VI)–tartaric acid system considerably different from that in the soil–Cr(VI)–oxalic acid system. As shown in Fig. 2, when tartaric acid was introduced to the soil–Cr(VI) system, Cr(VI) concentration in equilibrium solutions after 24 h was far less than that of tartaric acid-free system across the pH range investigated, which was more remarkable especially at low pH. For example, Cr(VI) existing in equilibrium solution of the ternary soil–Cr(VI)–tartaric acid system was 10.5 μ M, with 53.2 μ M in equilibrium solution of the soil–Cr(VI) system at the most acidic pH examined in this study. This indicated that soil surfaces catalyzed Cr(VI) reduction by tartaric acid occurred since there was no evidence for enhancement of Cr(VI) adsorption by the soil in the presence of tartaric acid. Because homogeneous reduction of Cr(VI) by tartaric acid in solutions across the pH wide in

this experiment proceeds very slowly and could be ignored, the observed acceleration of reduction reaction was owing to catalytic effects from the soil surfaces. Zhou et al. (2001) have also suggested that the soil colloids could act as a catalysts to speed up the reduction of Cr(VI) by *p*-methoxyphenol. The corresponding concentration of Cr(III) in equilibrium solutions was presented in Fig. 3.

Several mechanisms have been advanced for the catalytic effect of metal oxides and clay minerals (Stone and Torrents 1995; Deng and Stone 1996a, 1996b; Deng et al. 2003; Smolen et al. 2003). These included: (1) increasing the reactant reactivity through adsorption onto the surfaces;

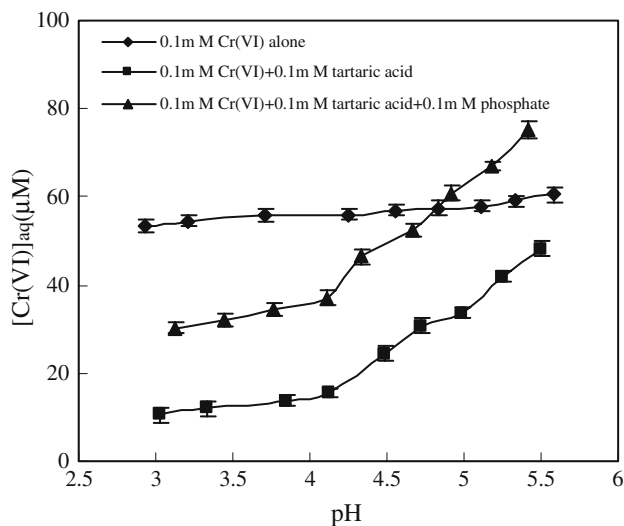


Fig. 2 Interaction between Cr(VI) and the soil in the presence of tartaric acid

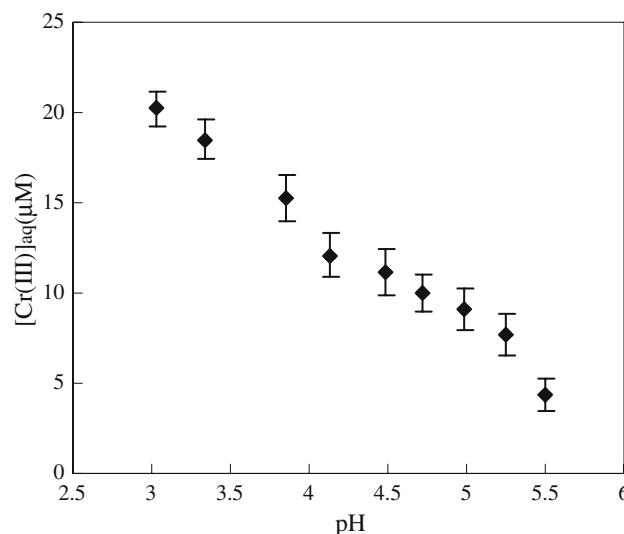


Fig. 3 Concentration of Cr(III) in equilibrium solutions of Cr(VI)–soil–tartaric acid system

(2) facilitating both reactants encounter and subsequent electron transfer through metal coordination; (3) redox cycle of active metals, like Fe(III)–Fe(II), acting as an electron shuttle between reductant and oxidant. Fe-oxides and clay minerals are included in the soil studied, and it might also be able to catalyze Cr(VI) reduction by tartaric acid through similar mechanisms mentioned above, which would be demonstrated as the following.

At present, it is still not possible to directly investigate the nature of adsorbed species pertinent to surface catalysis reactions (Stone and Torrents 1995), hence phosphate was chosen as a probe to test whether Cr(VI) reduction would be inhibited when the surface sites available for reactants adsorption were decreased by the competitive adsorption between reactants and phosphate. The results in turn could provide some indirect evidences for the mechanism that reactants adsorption was always a necessary step for the soil surface catalyzed Cr(VI) reduction to take place. Phosphate was selected because it has high affinity for soil surfaces and was commonly found in soil solutions. As shown in Fig. 2, although Cr(VI) concentration in equilibrium solutions of soil–Cr(VI)–tartaric acid system with addition of phosphate was still less than that of soil–Cr(VI) system at $\text{pH} < 4.84$, it was clearly higher than that of soil–Cr(VI)–tartaric acid system across the pH range examined. Studies have shown that phosphate suppressed Cr(VI) adsorption (Aide and Cummings 1997). So the observed inhibition of soil surfaces catalytic effect was obviously caused by the decrease in adsorption of Cr(VI) and tartaric acid. At $\text{pH} > 4.84$, both Cr(VI) and tartaric acid adsorption would be further suppressed because the shortage of available adsorption sites for either Cr(VI) or tartaric acid in the presence of phosphate might be intensified by the surfaces shifting to more negative. Therefore, Cr(VI) concentration in equilibrium solutions of soil–Cr(VI)–tartaric acid system with addition of phosphate was even higher than that of soil–Cr(VI) system at $\text{pH} > 4.84$ (Fig. 2), which obviously indicated that Cr(VI) reduction reactions might not occur virtually. Similar results were also obtained that the rate of TiO_2 -catalyzed reduction of Cr(VI) by mandelic acid was decreased in the presence of phosphate, which was believed to be caused by the decrease in surface sites available for reactants adsorption (Deng and Stone 1996a).

As shown in Fig. 4, a number of ferrous ions were released to solutions after the reaction between 1 g soil and 0.1 mM tartaric acid across the pH wide from 3.0 to 4.3 for 24 h. Total ferrous ions concentration in solutions ranged from 21.6 to 5.4 μM , and concentration of Fe(II) could be up to 13.8 μM . Thus, Cr(VI) could be directly reduced by Fe(II) existing in the soil solutions. According to Stumm and Sulzberger (1992), Fe(III) could facilitate electron transfer between organic compounds and Cr(VI) through

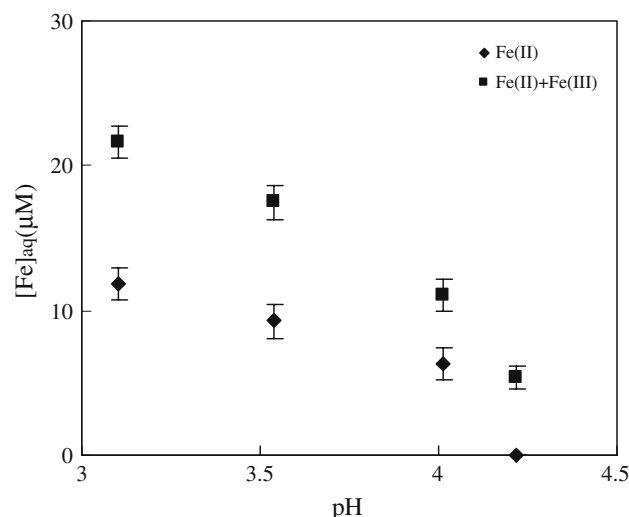


Fig. 4 Release of ferrous ions from tartaric acid promoted dissolution of the soil (Suspensions containing 1 g soil and 0.1 mM tartaric acid with total volume of 30 mL and reaction time was 24 h)

the formation of strong complexes with organic ligands and the existence of the Fe(III)–Fe(II) redox couple, acting as electron shuttles. Because high content of Fe oxides were included in the soil, the tartaric acid could promote release of Fe(III) to solution as well as the redox cycle of Fe(III)–Fe(II) through the reductive dissolution of Fe oxides by tartaric acid especially at low pH, which might be regarded as another mechanism for the soil surface catalytic effect. Previous studies have also demonstrated that reductive transformation of 4-cyanonitrobenzene would be promoted through the reductive dissolution of goethite by ascorbic acid (Smolen et al. 2003).

To further examine the role of Fe(III)–Fe(II) redox cycle in soil surface catalytic effect, a separate experiment was performed according to the similar procedures as those in Fig. 1, in which silica, instead of the soil, was used as adsorbent, with the suspensions containing silica + 0.1 mM Cr(VI), silica + 0.1 mM Cr(VI) + 0.1 mM tartaric acid, or silica + 0.1 mM Cr(VI) + 0.1 mM tartaric acid + 0.05 mM Fe(III). As shown in Fig. 5, the percentage of Cr(VI) adsorbed by silica in the absence of tartaric acid was below 10%, and Cr(VI) adsorption and reduction in ternary silica + Cr(VI) + tartaric acid systems was less than 20%, which indicated that the catalytic effect of silica surfaces was less than that observed with soil. While after addition of 0.05 mM Fe(III) to the ternary silica–Cr(VI)–tartaric acid systems, $[\text{Cr(VI)}]_{\text{aq}}$ was largely decreased, even below analytical detection limit of the method at low pH (3.35). So it was evident that the reduction of Cr(VI) by tartaric acid was very efficient in the presence of Fe(III), which in turn proved that Fe(III)–Fe(II) redox cycle could facilitate Cr(VI) reduction by tartaric acid in soils.

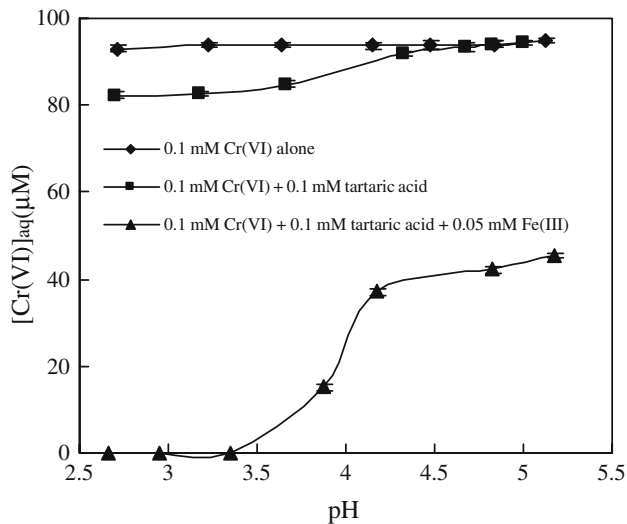


Fig. 5 Interaction between Cr(VI) and silica in the presence of tartaric acid and Fe(III)

Conclusions

Results from this study show that addition of oxalic acid would inhibit adsorption of Cr(VI) by the Fe-rich soil, thereby enhancing the mobility of Cr(VI) in the soil and ecological risk posed by the contaminant. Cr(VI) reduction by tartaric acid could be effectively catalyzed by the soil surfaces across the pH range (2.5–5.5) examined, which indicates that such biological reductant commonly present in soils could be used in remediation of Cr(VI)-contaminated soil.

References

Aide MT, Cummings MF (1997) The influence of pH and phosphorus on the adsorption of chromium(VI) on boehmite. *Soil Sci* 162:599–603

Chapman HD (1965) Cation exchange capacity. In: Black CA (ed) *Methods of soil analysis*. Amer Soc Agron Inc., Madison, pp 891–901

Deng B, Stone AT (1996a) Surface-catalyzed chromium(VI) reduction: the TiO₂-Cr^{VI}-mandelic acid system. *Environ Sci Technol* 30:463–472

Deng B, Stone AT (1996b) Surface-catalyzed chromium(VI) reduction: reactivity comparisons of different organic reductants and different oxide surfaces. *Environ Sci Technol* 30:2484–2494

Deng B, Lan L, Houston K, Brady PV (2003) Effects of clay minerals on Cr(VI) reduction by organic compounds. *Environ Monit Assess* 84:5–18

Fendorf SE (1995) Surface reactions of chromium in soils and waters *Geoderma* 67:55–71

Fritzen MB, Souza AJ, Silva TAG, Souza L, Nome RA, Fiedler HD, Nome F (2006) Distribution of hexavalent Cr species across the clay mineral surface–water interface. *J Colloid Interface Sci* 296:465–471

James BR, Barlett RJ (1983) Behavior of chromium in soils. VII. Adsorption and reduction of hexavalent forms. *J Environ Qual* 12:177–181

Jones DL (1998) Organic acids in the rhizosphere—a critical review. *Plant Soil* 205:25–44

Kotaś J, Stasicka Z (2000) Chromium occurrence in the environment and methods of its speciation. *Environ Pollut* 107:263–283

Loepper RL, Inskeep WP (1996) Iron. In: Sparks DL (ed) *Methods of soil analysis*. Soil Sci Soc Am Book Ser 5, SSSA, Madison, pp 639–664

Mehra OP, Jackson ML (1960) Iron Oxide removed from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner* 7:317–327

Mesuer K, Fish W (1992) Chromate and oxalate adsorption on goethite. 2. Surface complexation modeling of competitive adsorption. *Environ Sci Technol* 26:2365–2370

Nelson DW, Sommers LE (1996) Total carbon, organic carbon, and organic matter. In: Sparks DL (ed) *Methods of soil analysis*. Soil Sci Soc Am Book Ser 5, SSSA, Madison, pp 961–1010

Persson P, Axe K (2005) Adsorption of oxalate and malonate at the water-goethite interface: molecular surface speciation from IR spectroscopy. *Geochim Cosmochim Acta* 69:541–552

Smolen JM, McLaughlin MA, McNevin MJ, Haberle A, Swantek S (2003) Reductive dissolution of goethite and the subsequent transformation of 4-cyanonitrobenzene: role of ascorbic acid and pH. *Aquat Sci* 65:308–315

Stone AT, Torrents A (1995) The role of dissolved metals and metal-containing surfaces in catalyzing the hydrolysis of organic pollutants. In: Huang PM, Berthelin J, Bollag JM, McGill WB, Page AL (eds) *Environmental impact of soil component interactions, natural and anthropogenic organics*. CRC Press, Boca Raton, pp 275–298

Stumm W, Sulzberger B (1992) The cycling of iron in natural environments: considerations based on laboratory studies of heterogeneous redox processes. *Geochim Cosmochim Acta* 56:3233–3257

Tzou YM, Loeppert RH, Wang MK (2003) Light-catalyzed chromium(VI) reduction by organic compounds and soil minerals. *J Environ Qual* 32:2076–2084

Wittbrodt PR, Palmer CD (1996) Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances. *Environ Sci Technol* 30:2470–2477

Xu R, Zhao A, Ji G (2003) Effect of low-molecular-weight organic anions on surface charge of variable charge soils. *J Colloid Interface Sci* 264:322–326

Xu R, Li C, Ji G (2004) Effect of low-molecular-weight organic anions on electrokinetic properties of variable charge soils. *J Colloid Interface Sci* 277:243–247

Zachara JM, Cowan CE, Schmidt RL, Ainsworth CC (1988) Chromate adsorption by kaolinite. *Clays Clay Miner* 36:317–326

Zhou D, Chen H, Zheng C, Tu C (2001) Catalytic effect of soil colloids on the reaction between Cr^{VI} and *p*-methoxyphenol. *Environ Pollut* 111:75–81